

PATENT APPLICATION

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TITLE:

PCB SAMPLER

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PCB SAMPLER

10 FIELD OF THE INVENTION

A real-time PCB monitor consisting of a laser-induced vaporization and sampling cartridges coupling with a mobile GCMS system for determining PCBs on painted surfaces. The PCB monitor will be employed in the field for real-time determination and confirmation of the presence of PCBs in surfaces,
15 especially painted surfaces. This can eliminate the need and cost of sending samples to analytical laboratories for presence confirmation. The monitor is particularly useful in remote locations.

BACKGROUND OF THE INVENTION

20 In 1989 the Navy discovered during the course of normal occupational safety work at a shipyard that PCBs occurred in many plastics, rubbers, adhesives, gaskets and other commercial non-metal products used in Navy Ships. In the early 1990's the Navy initiated a sampling program for PCBs in ships. At that time it was discovered that much of the MIL-spec paint used
25 on ships contained PCB, added as a plasticizer and flame retardant. Further investigation found paint containing PCBs in many non-Navy facilities and structures.

DoD components, the Navy, the Air Force, the Army, the Marines and the Coast Guard use common specifications for paints on vehicles. The MIL
30 Specs are not differentiated by service. It is highly possible (very likely) that vehicles, facilities and structures of the other services may also contain PCB. In 1989 work also began, directed toward development of an international treaty that would ban the use of PCB and nine other chemicals in paint. Some of these other nine chemicals may also be present in mil-spec paint and

commercial structures such as bridges, towers and other structures that require protective paint. It was found that the magnitude of the problem for just PCB contamination was very large.

5 BRIEF DESCRIPTION OF THE INVENTION

Broadly, the invention herein discloses apparatus that includes the use of a laser to vaporize any analytes such as, but not limited to, PCB or PCB like compounds in a surface sample, the vapor is transported to a detection area and tested. Typically the system is sufficiently portable to take to a site and
10 acquire samples for analysis on site.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic drawing illustrating one typical embodiment of the invention.

15 Figure 2A, 2B, 2C, 2D, 2E, and 2F are various views of the body (or in some embodiments a portion of a typical frame.

Figures 3A and 3B are GC plots of the observation of PCB from Example 6 in which the cold trap was used.

Figures 4A and 4B show a GC plot for the observation of PCB.

20 Figures 5A and 5B show two chromatographs of Example 7

Figure 6 shows a chromatographic pattern of Arochlor 1254.

Figures 7A and 7B show the calibration pattern (left) as compared to the observed pattern on Sample 1(right).

25 Figures 8A and 8B show a comparison of mass spectrometry results at a retention time of 41.5 minutes.

Figure 9 is a schematic diagram showing another embodiment of the invention.

Figure 10 is a depiction of the collection head held against a surface and positioned to collect a sample.

30 Figure 11 is a depiction of a typical desorber measurement unit.

Figure 12 is a schematic drawing of the mirror assembly for the sample head. Laser light enters from the bottom from an optical fiber and interface

into a lens and then onto the mirror the light is then focused onto a target. Typically the mirror is controlled to scan a selected area typically a rectangle or square.

Figure 13 is a schematic diagram of a typical AC wiring diagram for the system.

Figure 14 is a graph showing a calibration and test curve for a preferred embodiment of the invention.

Figure 15 is a set of three mass spectra over of they type used to generate the calibration curve of Figure 14.

DETAILED DESCRIPTION OF THE INVENTION AND BEST MODE

In a first broad embodiment there is disclosed the use a laser to vaporize any PBC or PCB like compounds in a painted surface sample, a sample cartridge to absorbed the vapors. The absorbent trap is delivered to a heated system to desorb the vapors and to split the vapors to a mobile GC/MS system and to a vented system device. Typical equipment needed: Laser; GC/MS unit; EZ Flash unit; a heated cartridge device; a vented system; Helium Tank (99.99% pure); generator; dry ice/liquid nitrogen; Van; material for casing of sampling arm. This system is sufficiently portable to take to client site and acquire samples for analysis on site.

A second broad embodiment of the invention includes an in situ PCB analyzer/monitor that uses a miniaturized, handheld YAG laser to acquire samples from solid surfaces. Typically the system acquires samples as the YAG laser fires at the solid surface and vaporizes, dissociating the materials present to base materials (in the case of a ship, the hull), and produces a sample circumference of approximately 5 mm unfocused and about 0.3 mm focused in approximately 10 nanoseconds, with about 10 Joules of energy and a temperature between 3000 and 5000 degrees Kelvin. It is believed that this sample size will be sufficient for confirming the presence or absence of PCBs on solid surfaces. In addition, this system may be modified to identify materials, such as lead, chromate, or others, with properties that can be identified by using GC, MS, ICP, TAGA, ICP/MS, or FT-IR.

Typically when vaporized, the materials of concern are quickly drawn by a miniaturized diaphragm pump into a sample chamber (nominal size equivalent to that of a paintball chamber) that uses helium, nitrogen, or air as the inert carrier gas. This absorbent trap is then detached from the laser configuration and analyzed using a miniaturized, fast, field-portable GC/MS system (TDX EZ Flash™). This system analyzes for the constituent of concern (in this case, PCBs) and provides a printout or electronic results in approximately 10 minutes. The dissociation during sampling will provide the basis for identifying PCBs due to their unique nature.

Typically at the same time that the sample is acquired, a unique identification is given to each chamber sample and an auto engraving system identifies the wall surface with the sample number, which is also logged in on a read-only CD-ROM. Thus, there is no confusion regarding the identification of the sample. Additionally, it is planned that, at the same time the engraving is performed, the virtual coordinates of the sample will be identified on the test surface. This identification will be used to model the extent and location of the contamination and provide a virtual map to the sample locations.

Typically waste produced from this process is believed to be minimal due to the small volume required for a sample and the PCB collected is destroyed in the GC/MS. There is no extraction solvent waste generated, thereby reducing the volume of waste produced as part of the analytical process currently in use. It is projected that, by using this system to analyze for PCBs, the identification and reporting processes can be reduced from days/weeks/months to hours/days. This will provide clients cost savings by reducing wait time and management of areas not requiring decontamination.

Typical safety features of this system include two-stage interlock systems that make it difficult to inadvertently fire the system when not in proper position. Also, the second stage provides a red interlock light as a visual prompt to the technician that the system is ready to fire. Additionally, the system will not fire if the sample cartridge is not in position. This will help ensure that "valid" samples are acquired.

It is anticipated that one embodiment of a typical field-ready unit will be human platform operated (see Figure 1), meaning that the system is sufficiently compact for a human to carry to whatever location is needed without extensive support systems. The only field requirement will be a
5 constant uninterrupted power source. Gases such as nitrogen, helium or dry air that are needed to acquire samples can be contained in small unit-mounted pressure chambers (nominal size of 6 inches long and 2-3 inches in diameter).

Referring again to Figure 1, the sampling system 100 according to this
10 embodiment is placed on the surface to be sampled such as the hull of a ship 101 and held in place by pressure from shoulder pad 103. Ring pad 103 open in the center seals the sample area during the test. Power is provided through power connector 105. The sample is activated by trigger 107. On activation laser 109 is turned on and sends a beam 111 onto the test surface
15 101. As analyte is vaporized from heating and/or breakdown of the surface, gas from gas supply 113 enters the sample area through opening 115 and sweeps the analyte into opening 117 to the absorbent trap 119. A vacuum pump 121 typically aids in conducting the analyte carrying gas to the adsorbent trap 119. A quick release mechanism 123 for the adsorbent trap
20 aids in speeding up the process. For safety, activation of the laser is indicated to the user by an indicator such as laser activation light 131. A quick disconnect may also be provided for the gas supply but is not as critical.

In other embodiments, it is important to note the concept of collection rests on the principle that the flow of sample material should be directed to a
25 absorbent trap before the sample material has a chance to recombine and plate out on the walls. The stream is now sent straight to the collection filter placed only a short distance (2cm) from the chamber into which the laser ablates the surface paint. To avoid deposits on the walls of the collection device the body of the device is heated. ($T = 200^{\circ}\text{C}$ to 250°C). Typically, the
30 wall of the chamber is massive enough to provide heat energy that keeps much of the volatile ablated material in the vapor phase until it has been captured at the filter. Typically, the chamber is shaped so that make up

nitrogen or other inert gas will flow from the outside rim to the inside chamber, being heated as it moves. Typically, the outside rim has been made cool enough by the embodiment of the design so that the viton gasket can contact the wall without scorching or burning the sample surface (e.g. paint).

- 5 Typically, laser energy is provided for sample vaporization through a line intersecting with the plane of a viton gasket placed on the surface. This laser beam is provided with optics that can be adjusted to change the size of the ablated area (spot).

Referring now to Figure 2, this figure depicts the typical configuration
10 of the device at the time of the first tests. The main body of the device is typically aluminum or stainless steel. A Carbo trap tube was placed directly at the end of the hot cavity above the laser intersection with the center line of the device. The flow through the absorbent trap was powered by a diaphragm pump, which can be of fixed or variable speed. The filter
15 materials have been chosen to preferentially capture PCB. Heating lines to keep the collector near 300°C are used.

Tests of typical collection devices were made and tested: It was determined that the laser power being used in the early experimental tests was much higher than needed. Biphenylene, a combustion product of
20 polychlorinated biphenyls has been observed with observations of spiked samples at 160 ng/cm². Later tests produced observations of PCB directly in the collected samples. The sample collector has been made to work. Further details of the products and sample collection and detection are discussed below.

25 As discussed above, using a laser method for collecting vaporized analytes such as polychlorinated biphenyls (PCB) materials out of paint matrices is quite feasible. Typically an absorption trap preferentially collects the vaporized materials from the laser ablated sample.

The PCB materials were observed using gas chromatography/flame ion
30 ignition detector (GC/FID) and gas chromatography/mass spectrometry (GC/MS) techniques. The analyst can easily see the mass spectrometry ion

pattern produced by the PCBs due to the multiple chlorine mass losses at concentration well below 100 micrograms/100 cm². The patterns match the pattern of the calibration spectra of the Arochlor 1254 standard, a common mixture of PCBs. Quantitative work was limited to several levels of

- 5 contamination produced corresponding relative levels of identified PCB. The full quantitative database can be constructed following the teachings herein.

The need for separation of pollutants from a paint matrix is applicable to more than just PCB materials. There are at least nine other pollutants of interest on the international level.

- 10 There are many PCB contaminated surfaces on military equipment (planes, ships, submarines and transport vehicles) and buildings due to the fact that the PCBs have been used as a fire retardant and/or a plasticizer in the paint on this equipment. When taking the equipment out of service, in scrapping equipment, the presence of PCB must be known so that proper
15 disposition of the materials can be made under EPA regulations.

At present the Navy and MARAD has hundreds of ships scheduled for disposal. About 98% of the Navy ships contain PCB. The Navy is required to check all painted surfaces for PCB before any cutting is undertaken. In addition, EPA requires that every load of scrap steel that leaves a shipyard be
20 certified PCB free.

- Using present verification procedures, samples must be scraped from the painted surface, sent to a laboratory, where the chemical extraction techniques are performed to separate the PCB s from the polymeric constituents of the paints. This separation makes it possible to use the
25 standard GC and GC/MS procedures for the analysis. This laboratory analysis process is very slow (days-weeks) and requires delays in the fieldwork. These delays due to transportation time, sample handling time, analysis time and reporting time required for this process, add significant cost to the separations.

- 30 With the system disclosed herein, the sample will be analyzed in the field. Collection of the sample is performed by use of laser energy rather

than physically scraping off the materials and performing solvent extraction. A laser takes off the sample in such a way that the sample can be directly analyzed in the field using gas chromatographic and mass spectrometric techniques, and produces little to no hazardous waste.

- 5 The development of a near-real time PCB analysis system for painted surfaces is disclosed herein. According to the teachings herein, a near real time PCB analysis system using a novel laser sample collecting device will allow samples to be directly collected and analyzed in the field.

The envisioned method is to collect polychlorinated biphenyls (PCBs) by separation from other paint constituents using a laser ablation of the material. The technical goal is to use an energy density that does not destroy the PCB molecules and yet separates them from the polymeric constituents of paint. When the laser fires at the surface, the energy density causes the surface of the paint to be torn into pieces, which fly up into the collector's cavity. Some of the pieces are larger than molecules but at least some of the PCBs (at the right conditions) are broken into molecular sizes or at least become available for direct separation from the paint. GC/ECD and or GC/MS techniques can identify the separated molecular PCB constituents, or other definite markers for PCBs.

20 Once the PCBs have initially been separated, it is necessary that they be captured in a collection media without plating out on the walls of the collector. This implies that the collection system in front of the media must be heated since the vapor pressure of the PCB materials is very low at room temperature (only 760 torr at about 400°C.) Since the amount of material is a very low percentage of the paint, the temperature could be set near 200-300°C and full vaporization would still be achieved.

The system collects material over a set of areas on the surface, collecting for a specific number of pulses of the laser. In the first tests, the collector was mounted while the sample was moved under the intersection of the collector's laser beam. For example, for one sample collection, the laser was made to operate for 10 pulses (10 shots) on five different spots. (Early sample tests were used to indicate the extent of the sample collection needed for analysis).

The sample tube was then disconnected from the collector and was analyzed by a GC-MS instrument.

Fieldable GC-Mass spec instruments are available for in-field analysis. Once the PCBs in molecular form have been separated from the paint, the
5 tube can be carried a few meters (or many kilometers) after collection for the analysis. It is expected that the preferred method will be to make the measurement on-site for speed and convenience. After the collection, however, because the tubes contain solid room temperature PCB samples, it is not expected that there will be problems of sample degradation even in
10 transit to an off-site analyzer.

Each set of tests is made of 8-10 sample tubes collected, followed by the analyses. More than 50 total samples were analyzed.

It is noted that in some cases spiked samples were made rather than
15 using real analyzed samples obtained from ships. Several samples were made up with painted surfaces spiked with PCB Arochlor 1254.

Table 1. Benchmarks (Internal Deliverables)

No.	BENCHMARKS	PERFORMED
1	(Spiking Paint Samples in the Laboratory	Sample 1 (100micro grams /100 cm ²) Sample 2 (2mgm/100cm ²)
2	Run Test Samples (Test runs 1-3)	Yes
3	Review Preliminary Data from Test Run 1-3	Yes
4	Run Examples 4-7	Yes

5 There were two parts to the experimental set-up used in the Part 1 tests, the PCB sample collection and the PCB analysis equipment. The Part 1 goal was to prove the principle of the laser driven sample collection method and its interface to the GC-MS. The GC-MS analysis method needed to be modified only at its interface with the absorbent trap to allow the standard
10 GC-MS analysis to be made on the PCBs. The tubes are thermally desorbed to recover the samples. This sample is deposited at the entrance to the GC column. Therefore the analysis system used for the sample was not developed beyond this interface. This allows the use of standard GC-MS equipment as described in the analysis section below and interfaces with the
15 EPA standard method for measurement (<50 ppm present by weight in a GC measuremen).

Description of Samples

20 Sample 1 was made up with two surfaces. On one surface, paint with 100 ug/100 cm² PCB was applied. On the other surface only the non-PCB containing paint was applied. There were also several layers of paint below the first layer that were verified as being below the EPA Standard (less than 10 ug/100 cm² PCB contaminated). Care was taken to collect samples from

only the top layer by limiting the depth of sampling, controlling the number of laser shots on the sampling spots.

Sample 2 was made with surfaces of 1 mg/100 cm² and 2 mg/100 cm² and a third patch with only non-PCB containing paint. At first only a layer of
5 1 mg was painted on and analyzed in Example 5, but because variations were seen in collected material, an additional layer was analyzed in Examples 6 and 7.

Capture of the ablated material from the surface required the design and fabrication of a specialized surface collector. The purpose of the collector
10 is to capture all material ablated from the surface and transport it to the sorbent tube with minimum loss. Although not included explicitly as a benchmark in the original plan, the collector was determined to be a key element of the collection system. Figures 2A-F shows one embodiment of a frame for PCB collection. The body or frame of the collector is the heart of
15 the invention and is shown in the figures. The body is heated by four heated elements powered by a Variac set at about 50V (Setting 75). This device has several features which allow it to function as planned. The body of the device is heated to 250-300°C under operation. This heated section proved temperature stable under operation attached. The sample is pulled through
20 the cavity and through absorbent trap which functions as a molecular trap. In order to keep oxidizing combustion from the ablated sample, a stream of nitrogen was passed under the SS inner rim of the device to make up for the sample volume pumped through the tube. The flow was automatically adjusted to make up the sample flow assuring none of the sample was lost.
25 This nitrogen flow was later found to be unnecessary for PCB analysis but is useful in analytes that oxidize.

Figures 2A through 2 F show several faces of one embodiment of the frame for the sample collector. The optical interface of the laser with the collection system consists of a quartz window at about 45-degree angle from
30 the surface. The laser is directed at the surface and intersects it in the center of the collector.

The Laser enters from the back side through a window on the bottom

and intersects with the surface in the center of the cavity. The sample is drawn to the dark area in the upper part of the cavity. Makeup nitrogen flows under the wide rim where it is heated by the surface as it flows by.

The Laser used for ablation was a Continuum Model Surelite I Nd:Yag laser operating at 1.064 micrometers wavelength. Its energy was varied by adjusting the Q switch delay between 4mJ per pulse and 425 mJ per pulse. Its normal operation was at 10 pulses per second (10 Hz) but in order to test whether the sample needed to be cleared of the optical path in order to efficiently operate, it was also operated by manual trigger and at 0.5 Hz during some of the tests. This parameter did not product obvious changes in the results obtained. The laser size used is much larger than the laser expected to be used on the final system. In fact it is expected that a solid state laser of hand held size will be able to reach the energy density required. An alternative to a smaller laser is to couple this size laser to the collector by means of a fiber optic bundle. The latest embodiment has an energy of 40 mJ/pulse and is fiber optically coupled.

Analysis for PCBs

After the sample is collected, which takes from about 1- 3minutes for a tube, the sorbent tubes collecting the sample were disconnected, capped, and hand carried to the Atmospheric Sciences and Applied Technology Mass spectroscopy facility for analysis. The tubes used to analyze the paint materials were originally about 7 inch by 0.25 inch stainless steel tubes made by Supelco and shortened to about 4.5 inches. Carbotrap 200 (70/80 glass beads, 20/40 Carbotrap B, 68/80 Carbosieve SIII) was packed into the tubes as a collection medium.. Originally cleaned for 6 Hrs under nitrogen flow at 325°C, they could later be recleaned by the same technique performed for 2 hrs. The set was reused for each test.

During analysis, the sample tubes were individually placed in a small oven and thermally desorbed onto the GC trap at 275°C-300°C for 10 minutes with a nitrogen flow rate of about 35 cc/min. Several of the experiments were performed with this GC trap at room temperature because most if not all

of the PCB constituents are trapped in this 10°-20°C temperature because of their low vapor pressure. Other experiments were performed with this trap held at -100 C. Both worked but the room temperature trap holds only the low vapor pressure components effectively reducing the presence of high
5 vapor pressure compounds.

The GC trap is then heated to 300°C to transfer sample to the head of the column which is held at -50°C for 2 minutes. The temperature of the column is programmed to rise at 8°C/minute (or 15°C/minute) to 280°C and held for (18 minutes)-28 minutes. It took the PCBs about 40-50 minutes to
10 move through the column at the 8°C/minute rate of heating.

The instrument used for earlier analysis was the HP 5880 GC with FID and 5970 MSD with Chemstation software. This is not a state of the art system implying that there is room for engineering and cost considerations to be made when specifying the field system. The best technical system need
15 not be chosen for successful operation. Any commercially available system that can be used for EP8082 type work is sufficient.

The test matrices by sample are summarized in Table 4. In Table 4
20 sample measurements are labeled with test numbers and a letter designation (e.g., Example 7A.) At first, the amount of sample needed for the analysis was unknown, so in the first Examples there was an effort to vary collection parameters to ensure observation of enough material. Examples 3, 4 and 5 and 6 were run with a cold trap. With the cold trap operating, because of the
25 large amount of material traveling through the system, some of the mass spec runs were not successfully completed because they saturated the mass spectral instrumentation. (No mass spectrometry analysis for these runs was obtained). After Example 6 several calibration runs were made which proved that room temperature trapping at the GC trap at near room temperature also
30 worked well for capturing PCBs and that the cold trap might be a more complicated procedure than required.

Example 1 to Example 3 - - Initial Series of Examples

The laser power for Example 1 was 425 mJ per pulse focused on a spot of about 2mm diameter (Energy density about 10,000 mJ/cm²). Observation of Sample 1 was made. In this example series biphenylene in four times
5 greater amounts in the PCB contaminated samples than in the non-PCB contaminated samples was observed. Biphenylene is a structural relative to the biphenyl which is a structural relative of PCB. In this example a ramp time of 15°C/ minute for the GC was used. Besides the biphenylene, it was to be able to see PCB materials at ~26 minutes retention time. When analysis in
10 this period was done on the small peaks, the mass spectrometry instrument made no PCB identification. Nor did there seem to be a GC pattern in the region that was recognized as the PCB. It was concluded that there was a possibility that the PCB materials were being destroyed. Consequently, the laser power was lowered on the next set of examples. Note that depending
15 on the surfaces tested, a range of laser energy densities of about 1,000 mJ/cm² to about 100,000 mJ/cm² are possible with this laser device.

For Example 2, the laser power was 150 mJ per pulse (3000mJ/cm² per pulse) again focused on a spot of about ~2mm on Sample 1. In these examples again biphenylene in four times greater amounts were observed in
20 the PCB contaminated samples than in the non-PCB contaminated sample. Still no PCBs were observed.

In the Example 3 test, laser pulses of 4 mJ using the same lens position were used at the start, but this energy density was not enough to ablate the paint on Sample 1. This energy yielded no spot at all. The energy
25 for Example 3 was then raised to 19 mJ and 46mJ per pulse. Variations in the number of shots were made to compensate for the change in energy in order to obtain a constant amount of material for the analyses.

In the analysis there seemed to be more material, (but a cold trap is also being used to collect it at the GC in the belief that PCB material may be being
30 lost). The analysis in this example yielded the identification of biphenyl as well as biphenylene. The quantification of these runs showed a tendency to have higher biphenylene and biphenyl in the observations of the PCB

materials but the results did not yield as clear a ratio as did the higher powered examples. Looking back with 20-20 vision, these runs were still too short to observe PCBs which were later found to have had a longer retention time.

5 In Example 2 and Example 3 tests a ramp time of 8°C/ minute was inadvertently used instead of the intended setting of 15°C/min for the GC. This occurred because the system was automatically reset when the system failed at one point overnight. PCB materials were expected to be seen, however, no materials past the biphenylene peaks were found. There was a possibility that the PCB materials were being destroyed, but later it was found
10 that the inadvertent shift in the time by the automatic reset had pushed the PCBs out of the range and in fact out to past 40 minutes. It is possible that at these energy densities were not destroying the PCBs. This question, however, has not been pursued since the PCBs were observed at a lower
15 power density that is more advantageous anyway.

At the end of the initial runs PCBs were not identified directly, but it was felt that there was strong evidence that the presence of the PCB could be obtained by monitoring the biphenyl concentration. This evidence looked weaker as the energy of the laser was reduced. The presence of biphenylene
20 as a substitute for PCB was also not totally unambiguous because the measurements indicated that even in non-PCB containing paint there is some biphenylene and biphenyl present or produced by the process.

Example 4, 5 and 6

25 Sample 1 was again observed in Example 4 and was basically a repeat of Example 3. The energy was kept at 19 mJ per pulse in Example 4 in order to try to find the PCB materials directly. The analysis again yielded the identification of biphenyl as well as biphenylene. The quantification of this did not yield as clear a ratio of the two products between the PCB and Non-PCB
30 material as the higher-powered tests had shown. Looking back again with 20-20 vision these runs were 40 minutes in maximum retention time, still too short to observe PCBs and more material needed to be collected to see

Sample 1 under the conditions the GC was set at.

It was decided to spike a sample at high levels to aid in finding the PCB peaks. For Example 5, Sample 2 with PCB spiked at $1\text{mg}/100\text{ cm}^2$ was observed. For Example 5 the energy was also raised to $49\text{ mJ}/\text{pulse}$. The paint layer was too thin and the sampler was going completely through the layer of paint. This layer was not very even. The quantification of this did not yield as clear a ratio of the products biphenyl and biphenylene as the higher powered tests with the thicker layers. This phenomenon was attributed to the uneven layers of paint. Some of these runs were 50 minutes long rather than 40 minutes. Having noted that the runs might be too short, after the first few tubes, the maximum retention time of 40 minutes was extended to 50 minutes. At first, -the small differences in the peaks in this later time region was not noted, but on reanalysis direct evidence of PCBs was found in the long runs of Example 5. directly in the CG-MS Spectrum

Several other points of worry were investigated in Example 5. First, it was verified that the cleaned tubes were actually clean. An unopened tube run as if it had been used for collection produced an almost perfectly clean GC scan. Second, a test on a tube that was opened and exposed to flow without use of the laser produced a surprising amount of material when the collector was placed over the top of the PCB surface. At this point the question of air cleanliness was raised. This later was dispelled when it was found that there was very little response from a tube that had been collecting for two minutes away from the surface in Example 6.

Example 6

For Example 6 more spiked paint was added on the PCB layer of Sample 2 and also more clean paint was added on the non-PCB layer. The PCB level on Sample 2 was $2\text{mg}/100\text{cm}^2$. All examples were collected using 49 mJ per pulse 10 shots on 10 spots. For the first time it was noticed that there were small eluting components at times between 40 and 50 minutes retention time in the PCB runs that were not in the non-PCB exposed samples. These are seen in the right scan of Figure 3A and 3B past 40 minutes.

Mass spectrometry identification yields a pattern that is observable 154 biphenyl, 185 chlorobiphenyl, 220 bi-chlorobiphenyl and 254 tri-chlorobiphenyl, and 290-292 quadra-biphenyl isomers. Figures 4A and 4B show this pattern in a calibration spectrum of PCB being detected at one
5 retention time. This pattern is compared in the same figure to the pattern at the same retention time of the Arochlor 1254 calibration run. They match. In Example 6 quantification using the mass spectrometry abundances was shown also by an analysis using a normalization of the amount of material in peaks 28 minutes to 39 minutes and rationing the PCBs seen from 40 minutes
10 to 47 minutes to them. PCBs are present after 40 minutes and in fact are consistent with the calibration run performed after this run. Three distinct levels were observed, after subtracting out the background levels. This shows the possibility of the quantified operation.

Since PCBs are observed only in the later retention times and nothing was
15 analyzed earlier, it was decided that too much material was being collected in the early part of the run. In Figures 3A and 3B, the observation of PCB from Examples 6 in which the cold trap was used and Example 7 in which the room temperature trap was used to collect the PCB materials, letting lighter higher vapor pressure components be driven from the trap before the start of the GC
20 run. This led to the conclusion that a cold trap was not necessary.

Referring now to Figures 3A and 3B, Figures 3A (left) and 3B (right) shows the difference in the GC Runs when using a cold trap as in Example 6 at right and the relative cleanliness of the warm trap collection of the PCBs at left.
25 PCB are the main constituents not lost or at least partially recovered with the warm trap. Note chromatogram at right is 10X the scale of the left.

The spectrum at left is the ion abundance scan of Arochlor 1254 calibration of Example 7 at a retention time of 41.5 minutes. The right spectrum shows the observation of 5 cm²) 100 micro gms/100 cm² (Sample
30 1) at the same retention time. Both spectra show the ion spacing pattern of successive lost chlorine atoms from multichlorinated isomers of PCB.

Example 7

Whether collection was affected by retention time and multiple pulses of the laser on the ablated material in transit was tested. Several runs were made with and without the PCBs on Sample 2. Some of the runs were made
5 at 10 Hz (pps) and some of the runs were made at 0.5 Hz with all the other conditions being the same. The number of pulses per second appeared to make no difference at all in the amount of material collected or PCB observed.

The next question had to do with the level that could be observed. Sample 1 observations were also made and compared to Sample 2
10 measurements.

Results of Comparison of Sample 2 PCB at 2mg/100 cm² with Background Sample 2 Observations

15 Keeping the same energy density, it was decided to increase the spot size so that the material could be collected faster. This was particularly necessary in the subsequent measurements on Sample 1 in which the concentration was nearer the lower detection limit of the technique. Using the energy density that was found to work in the previous experiments, observations were made
20 on Sample 2. Sample 2 is the 2mg/100 cm² spiked Sample 5. The spot size for Example 7 was approximately 5 times the spot size of the previous examples. Area was about 0.2 cm² per spot. Spots covering a total area of about 1 cm² were observed for each sample tube collected, on both the PCB contaminated area and

25 Figures 5A and 5B show two chromatographs of Example 7 observing the Sample 2 PCB (2 mg/100 cm²) observation with a test on a sample from the Sample 2 non-PCB surface. Background levels indicate that this pattern could be seen below 0.5 mg/100 cm² the Non-PCB contaminated area. The scans in Figures 5A and 5B show comparison scans of PCB (left) versus non-
30 PCB (right). The pattern of the lines in Figure 5A at left are equivalent in shape to the pattern seen in the calibration run of Arochlor 1254 shown in Figure 6. Figure 6 shows the Abundance level versus the Retention time

observed for a 5 micro-gram sample of PCB Arochlor 1254 used as a calibration point. Features after 40 minutes are all PCB isomer elutions. Figure 6 shows a chromatographic pattern of Arochlor 1254 which looks like an equivalent pattern to the sample of PCB observed in Figures 5A and 5B.

5 Table 2 shows the results of an analysis of the total ions at retention times corresponding to the time period the PCB isomers are eluted from the GC. At this high concentration there are no interfering peaks. Observation of the peaks at a sampling of retention times indicates that the PCB peaks can be distinguished from the interferences. The pattern of ions near 292,
10 256,220,185 and 154 were observed in the contaminated peaks and found to be absent in the background sample. Abundances of this ion pattern compounds in the background are absent. There are only very small features in the background runs observed.

15 Table 2. Total Ion Observations of Sample 2 at Retention times in the Calibration Period

Retention Times Minutes	Calibration Run Relative Peak Height Total Ion	No PCB Relative Peak Height Total Ion	Mass Spec Pattern Confirmation Indicates	PCB 2100ug/100 cm ² Relative Peak Height Total Ion	Mass Spec Pattern Confirmation Indicates
41.48	8			1.	Yes
41.62	3	0.7	No		
42.02	5	0.3	No	0.05	Yes
42.73				0.2	No
42.81				0.8	No
43.02	4.5			0.05	Yes
43.16	8		No	0.05	Yes
43.69		0.7			
43.76	7.5	0.1	No	1.0	Not All
44.46	4.5	0.01			
44.75	6			0.03	Yes
45.51	4	0.03	No		
46.30	3.5				

Results of Comparison of Sample 1 PCB at 100 ug/100 cm² with Background

20

Sample 1 Observations

Using the energy density (1000 mJ/cm²) that was found to work in the

previous experiments, observations were made on Sample 1. Twenty-five Spots covering a total area of 5 cm² were observed, on both the PCB contaminated area and the Non-PCB contaminated area. The large number of spots were observed because it is necessary to collect more material to
5 ensure an acceptable signal to noise at this low concentration. This is an indication of the amount of area on which the measurement needs to be made for a successful field measurement with this GC-MS device. Later experiments with newer equipment allowed smaller sample sizes.

Figures 7A (left) and 7B (right) show the calibration pattern (left) as
10 compared to the Observed pattern on Sample 1(right). Figures 8A (left) and 8B (right) show an example of the results of an analysis of the total ions at retention times corresponding to the time period the PCB isomers are eluted from the GC. At this low concentration there are interfering background and some additional peaks in the region. Observation of the peaks at PCB
15 retention times indicates that the PCB peaks can be distinguished from the interferences. The pattern of ions near 290,254,220,185 and 154 were observed in the sample contaminated with PCB and found to be absent in the background sample as shown at right.

Figures 7A (left) and 7B (right) show the PCB eluting region of the
20 calibration run (5 micrograms Arochlor 1254). At right is the PCB region of the (Sample 1) chromatogram showing PCB peaks. Note that the strong continuous background, likely due to varying length chains of hydrocarbons is easily subtracted off.

Figures 8A (left) and 8B (right) show a comparison of mass
25 spectrometry results at retention time 41.5 minutes. On the left is shown the Sample 1 PCB observation. On the right is the non-PCB paint background. Note that the pattern for PCB observation is present at left.

Table 3 gives a summary of the mass spec confirmation and non-confirmation of the PCB pattern for each peak observed. There is more
30 ambiguity in this set but the PCB identification is still clear at the stronger peaks.

Table 3. Total Ion Observations of Sample 1 at Retention times in the PCB Region

Retention Times Minutes	Calibration Run Relative Peak Height Total Ion	No PCB Relative Peak Height Total Ion	Mass Spec Pattern Confirmation Indicates	PCB 100ug/100cm ² Relative Peak Height Total Ion	Mass Spec Pattern Confirmation Indicates
41.48	8			1.	Yes
41.62	3	0.7	No		
42.02	5	0.3	No	0.05	Yes
42.73				0.2	No
42.81				0.8	No
43.02	4.5			0.05	Yes
43.16	8		No	0.05	Yes
43.69		0.7			
43.76	7.5	0.1	No	1.0	Not All
44.46	4.5	0.01			
44.75	6			0.03	Yes
45.51	4	0.03	No		
46.30	3.5				

Technical Conclusion and Recommendations

- 5 Using a laser method for collecting PCB materials out of paint matrices is quite feasible. It was observed that the PCB materials using GC/FID techniques at 2 mg/100 cm² level with high signal to noise. Based on results of measurements on Sample 2 it was estimated that the GC area might be sufficient for the identification with concentrations as low as 500
- 10 micrograms/100 cm². Data collected on Example 7 Sample 1 show that using GC/MS one can identify PCB materials in paint at levels below about 100 ug/100 cm², although some future work will have to be performed that will automate the pattern recognition. The analyst can easily see, at concentrations well below 100micrograms/100 cm², the mass
- 15 spectrometry ion pattern produced by the PCBs due to the multiple chlorine ion mass loss. These patterns match the calibration spectra for the Arochlor 1254 standard. It also has been demonstrated by Example 6 data that this collection can be performed quantitatively. Further, a collector was build that would operate well as a field system, and a
- 20 absorbent trap that preferentially collects the PCB materials.

Table 4. Summary Table of Samples Observed.

	Laser Power	Shots	Spo ts	Dia mm	T °C	Sample	PCB s Obs erve d	Markers Observed	Retent ion	M ass Sp ec	Tube	GC or MS Identifi- cation
Test Set 1	472mJ	Varied (V)	5	V	269	Sample1 (100micro-gm/decimeter)	No	No Analysis	---	--	-	-----
Test 1a	472	25	10 (2)	2		Sample1-PCB)	No	Material-biphenylene	40	No PCB	L006	5880AROC. 15R
Test 1b	472	25	10	2		Sample1-PCB	No	Material-biphenylene	40	No PCB	L004	5880AROC. 16R
Test 1c	472	25	10	2	276	Sample1-PCB	No	Material and less biphenylene	40	No PCB	L011	5880AROC 17
Test 1D	472					Sample1-PCB	No	Material-biphenylene	40		L001	5880ARO C18R
Test 1E	472					Sample 1 New Paint No PCB Sample 1	No	Material and less biphenylene	40		L011	5880ARO C20R
Test 2a	152	25	4	2	268	Sample 1 PCB	No	Materials and less biphenylene	40		L004	588AROC 21
Test 2b	152	25	4	2	263	Sample 1 No PCB	No	biphenylene	40		L006	588AROC 22R
Test 2c						Sample 1 PCB	No	biphenylene	40		L001	5880ARO C.23R
Test 3a	4mj	25				Sample 1 PCB	No	-No analysis-	40		---	-----
Test 3b	19mj	100	10			Sample 1 PCB	No	Biphenylene (BPNLene) and Bi Phenyl(B PNL)	40		L001	AC060701.0 4R-mass spectrometry
Test 3c	19	100	10			Sample 1 No PCB	No	BPNLene & BPNL			L004	AC060701.0 3R
Test 3D	19	200	10			Sample 1 PCB	No	BPNLene & BPNL			L006	AC060701.0 5R
Test 3E	19	200	10			Sample 1 No PCB	No	BPNLene & BPNL			L011	AC060701.0 1R
Test 3F	19	200	10			Sample 1 No PCB	No	BPNLene & BPNL			L008	AC060701.0 2R
Test 3G	46	100	10			Sample 1 No PCB	No	BPNLene & BPNL			L012	AC060701.0 6R
Test 3H	46	100	10			Sample 1 PCB	No	BPNLene & BPNL			L005	AC060701.0 7R
Test	19mj	25				Sample 1	No	BPNLene	40		L010	AC061901.0

4a						100ug/deciliter		&BPNL				1R
Test 4b	19mj	25				Sample 1 PCB	No	BPNLene &BPNL	40		L002	AC061901.0 2R
Test 4c	19mJ	100				Sample 1 No PCB	No	BPNLene &BPNL			L007	AC061901.0 3R
Test 4D	19mJ	100					No	BPNLene &BPNL			L009	AC061901.0 4R
Test 4E	19	200					No	BPNLene &BPNL			L008	AC061901.0 5R
Test 4F	19	200					No	BPNLene &BPNL			L011	AC061901.0 6R
Test 4G	19	200					No	BPNLene &BPNL			L004	AC061901.0 7R
Test 4H	19	100					No	BPNLene &BPNL			L001	AC061901.0 8R
Test 5A	0	--	--	275 9		Over the Top of Sample 1 PCB		No PCB			L010	AC062701.0 1R
Test 5B	49	20	5	275		Sample 1 All -PCB		PCB			L001	AC062701.0 2R
Test 5CE	49	20	5	272		Sample 1 All PCB		PCB			L012	AC062701.0 8R
Test 5D	49	20	5	273		Sample 1 All Paint-NoPCB		No PCB			L004	AC062701.0 3R
Test 5E	49	20	5	272		Sample 1 All Paint-No PCB		No PCB			L005	AC062701.0 5R
Test 5F	49	20	5	273		Sample 1 Paint3-PCB2		PCB			L009	AC062701.0 4R
Test 5G	49	20	5	272		Sample 1 All Paint 2-PCB 3		PCB			L007	AC062701.0 6R
Test 5H	49	20	5	272		Sample 1 Paint3-PCB2		PCB			L011	AC062701.0 7R
Test 5I	49					Sample 1 Paint2-PCB3		PCB			L008	AC062701.0 9R
Test 5J	Blank					Tube Blank		No PCB			L002	AC062701.0 10R
Test 6A	49	10 (10/s)	10	274		Sample 2 Paint-	Yes	No PCB	50		L007	AC071601.0 1R
Test 6B	490	10 (10/s)	10	269		Sample 2 Paint	Yes	No PCB	50		L011	AC071601.0 2R
Test 6C	49	10 (10/s)	10	270		Sample 2 Half Paint-PCB	Yes	PCB	50	PCB	L009	AC071601.0 3R
Test 6D	49	10 (10/s)	10	266		Sample 2 Paint-PCB	Yes	PCB	50		L004	AC071601.0 4R
Test 6E	49	10 (10/s)	10	267		Sample 2 Paint-PCB	Yes	PCB	50		L012	AC071601.0 5R
Test 6F	49	10 (10/s)	10			Sample 2 HalfPaint-PCB	Yes	PCB	50		L008	AC071601.0 6R
Test 6G	---	0		RT		Room Air	No	No PCB	50	No PCB	L005	AC071601.0 7R

Test 6H	---	0		270		Over Sample 2	No	No PCB	50	Material No PCB	L001	AC071601.0 8R
Test 6I	---	0		RT		NOT OPENED	No	No PCB	50	No PCB	L006	AC071601.0 9R
Test 6J	---			270		Over Sample 2 Paint after cleaning	No	No PCB	50	Material No PCB	L010	AC071601.0 10R
Test 7A	218	10 (10/s)	5	275		Sample 2 Paint	No	No PCB	50	No PCB	L009	AC072401.1 0R
Test 7B	218	10 (10/s)	5	263		Sample 2 Paint	No	No PCB	50	No PCB	L011	AC072401.0 3R
Test 7C	218	10(10/s)	5	257		Sample 2 Paint-PCB	Yes	PCB	50	PCB	L005	AC072401.0 2 R
Test 7D	218	10 (10/s)	5	254		Sample 2 Paint-PCB	Yes	PCB	50	PCB	L004	AC072401.0 9R
Test 7E	218	10 (0.5/s)	5	251		Sample 2 Paint-PCB	Yes	PCB	50	PCB	L012	AC072401.0 8R
Test 7F	218	10 (0.5/s)	5	257		Sample 2 Paint-PCB	Yes	PCB	50	PCB	L006	AC072401.0 4R
Test 7G	218	10 (0.5/s)	5	255		Sample 2 Paint	No	No PCB	50	No PCB	L008	AC072401.0 5R
Test 7H	218	10 (0.5/s)	25	260		Sample 1 (100micro-gm/decimeter)	Yes	PCB	50	PCB	L001	AC072401.0 6R
Test 7I	218	10 (0.5/s)	25	275		Sample 1 (100micro-gm/decimeter)	No	No PCB	50	No PCB	L010	AC072401.0 7R
Test 7J	Calib	1	0	---	---	5ug Arochlor 1254	5ug Arochlor 1254	PCB Standard	50	PCB	L007	AC072401.0 1R

Referring now to Figure 9, a further embodiment of the invention is an

5 analyte (e.g. PCB) analytical system. Typically a full version of the analytical system consists of a sample module 900 (sampling head 910, see Figures 9 and 10, and control assembly, see Figure 9) and the analytical assembly module, see Figure 11. The sampling head 910 is typically hand held or surface mounted and used to collect the surface samples from various

10 surfaces 960. The control module 980 is typically mounted on a cart 981 or carried into the sample area by hand (e.g. suitcase size modules) or by trailer

and provides various devices such as pumps, logic modules, temperature controllers and temperature monitors. Mounted in the cart is typically a laser unit 982 that provides a laser beam for the sampling head via an optic cable 970. The laser is typically a Nd:Yag laser operating at 1064 nm, providing
5 energy at up to 5 pulses per second at an energy of about 40 mJ per pulse. Other cables 972 may be used for communication or power supply between the sample head 910 and the control module 980. The bottom unit in the cart is typically a controller 983 such as a Sierra Instrument Newport ESP-300 Controller.

10 Referring now to Figure 10, there is shown a detailed view of the sampling head 910. Typically the unit comprises a frame 1001 for holding and the various parts and for forming an enclosed volume 1003 where the sampling takes place. The sample head 910 is typically placed against a surface 1005 so that the open end 1007 of enclosed volume 1003 touches the
15 surface 1005. A mirror control assembly 1010 provides control of a laser beam 1011 that provides the energy for vaporizing a sample analyte. Typically a transparent window 1113 (CVI W2-PW-1025-C-1064-0) is used to shield the mirror control assembly from any contaminants generated by the laser at the surface. Laser beam focusing lens 1115 may or may not be
20 needed. When a sample is ready to be collected by generation of vaporized analyte the surface a flow of gas from gas line 1120 at opening 1121 sweeps the analyte into a second opening 1123 leading to adsorbent trap 1130. Adsorbent trap 1130 is typically held in place by disconnects 1131 that may be quick disconnects to allow fast operation of the unit. A gas line 1133 leads
25 via a line in the cable 972 to the controller module 980 where a vacuum pump not shown can be used to augment gas flow. Typically the pump provides a speed for air through the sampling chamber of about 500 ml per second. Various gases may be used, with PCBs it was determined that ordinary air worked well, however in some situations inert gases may be
30 needed. Thermocouples 1140 are typically used to control and monitor temperatures at the sampling head 910. Heaters 1150 are used to maintain the temperature of the sampling head particularly in the sample collection

area to that required to prevent condensation of analyte and thus loss of sensitivity of the unit. The heater provides energy to the optical cavity in the sampling head to drive the temperature to about 230°C in the case of PCB measurement. The temperature controller is also located in the cart 981 and
5 receives information from/to thermocouples in the sampling head 910. A magnetic holder 1160 may be used to hold the unit to magnetic surfaces thus facilitating measurements.

As sample collection begins the laser pulses sending energy (the dotted line) to the surface that breaks the bonds in the paint releasing vaporized
10 material and small particulate that is then collected in an absorbent trap 1130. The absorbent trap is seen on the top of the sampling head 910 in Figure 10 and is connected to the pump and the outflow area of the optical cavity. The cavity is heated to about 230°C which ideally eliminates all deposits on the walls of the chamber and the optical window. Deposits are minimized by the
15 heating of the chamber, and by the flow of the gas that drives the vaporized sample into the absorption trap

Typically there is a hot air flow from preheated inflow openings into the sampling head that sweeps past the area heated by the laser beam and sweeps the gases generated by the heat from the laser beam into an outflow
20 opening to absorption trap where the gases of interest are absorbed or adsorbed onto the inner surface of the trap. A pump in the control module provides the required air flow.

Referring now to Figure 11, the sample spot is typically heated until a selected volume of paint or other surface has been removed. The absorption
25 trap 1130 is then removed from the sampling head 910 and is placed into thermal desorption unit 1180. The desorbed analyte then flows via line 1181 to analyte measurement unit 1190 which is typically a gas chromatograph 1191 and mass spectrometer 1192. Typical analyzing apparatus includes GC-MS; GC; I.R., infrared, analysis; nuclear techniques, e.g. Geiger counter; etc.
30 A currently preferred test spot size is about 0.01 cm² where the energy density is typically about 40 mJ/pulse. This is about 4000 mJ/cm² and works

for typical paints. This spot is scanned across the surface to strip an area of about 3mm by 3mm.

In a preferred embodiment the sample head 910 is connected to the control module 980 by a utility cable that consists of two gas lines for bringing
5 gas flow to the sample head 910 and back out for analysis, two control lines for motion of control of the scanning mirror 1109, two lines for the thermocouples 1140 in the front part of the sampler and power for heaters 1150 in the sampler.

Referring now to Figure 12, the figure shows the inner schematic view
10 of the optical related components in the sampling head 910. The sampling head consists of components that provide energy to the surface for stripping the top layer containing the impurity, and provides the sample collecting components. In order to reduce the size of the laser needed to provide the proper amount of sample for the analysis, the beam is sequentially scanned
15 over an area on the surface being analyzed. The scanning is accomplished by tilting the mirror 1109 placed in front of a fiber optic tip. The tip directs the energy through a lens which focuses it on the surface. The tilting mirror 1109 is programmed to cover a specified area. The area it covers, depends on the thickness of the paint layer to be analyzed. This is determined by the
20 operator before the sample collection begins.

Figure 12 details include the mirror control assembly 1110 typically consisting of mirror motion control units 1210 (Newport CMA -12CCCL, Newport U100-A38) a mirror head assembly 1220 (Newport UPA-45D1) holding the mirror 1109 (Newport 10QM2OHM.15). The lens used was a CVI
25 PLCX-25.4-19.6-UV-1064 type. An optical interface 1230 (Oz Optics HPUCO-25-1064-M-4.5AS-SP) was used at the end of the fiber optic cable 1240.

Referring now to Figure 13, the figure illustrates the electrical and logic connections for control of the sampling head. The figure is generally self explanatory.

30

Operating Procedures for the Sample Module

In the field, the apparatus is taken to the site of interest and the following steps taken:

1. Measure thickness of the paint. This typically is performed by use of a magnetic sensor made by Electro-phsik, the model minitest 4000. This instrument has heads for both magnetic material subsurfaces and conducting subsurfaces. On non-metallic surfaces the operator might use depth gages or acoustical sensing. The accuracy of the calibration requires this depth determination.
2. Carefully remove the sampling collector assembly (sampling head) from the container and place on site for use. Mount the absorbent trap into position using the quick connect feature. Record the tube identification and sample site identification.
3. Mount the sampling head to the area of interest. If the sampling area is steel or other magnetic material a magnetic holder may be used.
4. Turn on the heating system about 5 minutes before sampling. The heating system is started so that the sampling head is at operating temperature (for PCBs at about 225°C. When moving from site to site this may be already hot.
- 5 Check that the vacuum pump is turned on.
5. Run the program for controlling the laser and check the homing position of the laser. Calculate the target area = paint volume /thickness of the paint.
6. Typically, a selected volume of paint will be needed for measurement. Typically this is about (2mm³) Given the target paint volume desired the area to be sampled is determined by the above equation. Choose the area.
- 7 Run the sampling program which starts the laser Start the Laser
- 8 Typically the sampling takes about 5 minutes. Remove the absorbent trap. Cap it send it for analysis.
- 9 Replace the sample head into the controller cart.
- 10 Move the Sample Module to the next sampling site.

Typically the process will take about 10 minutes.

Analysis of the Samples for a preferred Embodiment of Invention

Equipment used in the latest and best embodiment of the Analysis

5 Assembly system is described in the following paragraphs. This system was used to analyze the samples of the latest PCB Sample Analysis Module described above. The Absorbent traps from the Sample Module measurements are transferred to the analysis instrumentation. The data from the absorbent traps and the paint thicknesses and volumes can be combined
10 to show a nominally linear relationship of mass detected and concentration in the paint.

The absorbent traps used are custom made, prepacked, ATD Tubes.(Perkin Elmer type) from Supelco. The tubes are packed with
15 CarboTrap 202., a Carbo Pack B. These tubes are cleaned in a Varian TC oven by precleaning the open tubes for several hours by simple heating to 340 C and by flowing purified nitrogen gas through the tubes for two hours at 100cc/min at this same temperature. The tubes are thus reuseable.

After the samples are taken to the sampling instrument the absorbent
20 trap brought to the Analysis Instrumentation. The tubes are uncapped and a small piece of glass wool is placed in the tip to prevent small particulate from entering the GC apparatus as the tube is desorbed. The absorbent traps are then were mounted in the Unity Markes Thermal desorber and raised to about 225°C. The desorber was used in split mode (2/1) where the sample for
25 analysis was transferred to the Inlet trap of the Gas chromatograph(GC) system.

The GC system is an HP6890 Series configured with a DB-5MS Column. The column is 60 meters long with an ID of 0.32mm and a 0.25micrometer film thickness. The temperature of the column was increased from 30°C to
30 220°C over a 50 minute period this time period. The output from this included PCB materials which were found to have retention times of about 25 minutes to 40 minutes.

The GC is coupled with a Mass Selective Detector an HP 5973 system. This system makes frequent measurements of the total mass spectrum at frequent times through out the retention time cycle. Unity Software was used with the HP5973 for control.

5 The Chemstation software was used to manipulate the MS output enabling analysis of specific masses for patterns verifying the presence of the PCB congeners. For example, peaks present at masses 360, 326, 292, 254, 222 are all multiples of the average chlorine isotopic masses. By looking at these ions the recognizable PCB patterns are observed. Figure 15 shows
10 three examples of these. The output of samples from materials containing PCB were analyzed as containing tetrachlorobiphenyls, pentachlorobiphenyls and hexachlorobiphenyls. Figure 15 shows a scan of these PCBs identifying the bands used in the materials scans to determine the quantification of the PCBs. Tetra chlorbiphenyls are seen at 25.5 minutes in ion 292, a group of
15 pentachloro congeners are seen at 31.3 minutes and 32.6 minutes in the ion of 326. The peak at 33.6 minutes contains hexachlorobiphenyl congeners as shown when looking at ion 360.

Referring now to Figure 14, the most recent and preferred embodiment for the invention was used to generate the depicted calibration curve and is
20 shown to indicate the state of the art in the development of the technique. A set of calibration standards were developed in which known amounts of PCB 1254 were mixed with the paint before being applied to the surface. The measured masses were combined with an epoxy paint and an anti fouling paint. To generate the data shown here several measurements at 10 ppm,
25 35 ppm, 60 ppm, and 110 ppm and 210 ppm were made on the paints. Points on this curve were determinations of quantity based on peak areas in bands as shown in Figure 15 using the four sets of bands representing the tetra, penta and hexa congeners. Each scan generates four points on the graph. Comparisons of the materials were made against the observations of
30 Pure Aroclor 1254. So that a concentration is determined by its relative band strength to the pure compound. Other controls on the experiments included internal standards such as phenanthrene injection into the tubes.

Referring again to Figure 14, in these measurements, the errors are in the measured mass for generation of the curve. The projection of these errors on the calibration curve, show the size of the error in ppm expected for a sample when this curve is used. The resulting error blocked out as the

5 indeterminate region in the measurements is two standard deviations of the error bars in the region of interest which is centered at 50 ppm. The EPA allowable standard for calling a sample uncontaminated is at 50ppm. Using or normalizing to a standard sample size (for example normalized collection volume (2 mm³) of paint) , the calibration curve using Aroclor 1254

10 standards indicated that for both of these paints within measurement error

- Detection of less than 100 ng PCB (Equivalent Aroclor 1254) material indicates the sample is clean.
- Detection of more than 290 ng of PCB materials indicates the sample is contaminated.
- 15 • Detection of levels between 100 and 290 ng indicates an indeterminate answer to the categorization of the painted surface. The surface then requires further testing. Either

The suggestion is to

1. Take a second sample on the area. (This might act a tie breaker)
- 20 OR
2. Send out a sample for standard analysis.

Note that the standard analysis may actually be no more accurate that this original measurement.

25

While the forms of the invention herein disclosed constitute presently preferred embodiments, many others are possible. It is not intended herein to mention all of the possible equivalent forms or ramifications of the invention. It is to be understood that the terms used herein are merely

30 descriptive, rather than limiting, and that various changes may be made without departing from the spirit of the scope of the invention.